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A review on operating parameters for optimum liquid oil yield in biomass pyrolysis

Javaid Akhtar [a,b,*], NorAishah Saidina Amin [b,1]

[a] Centre for Coal Technology, University of the Punjab, Lahore, Pakistan
[b] Chemical Reaction Engineering Group (CREG), Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai Johor, Malaysia

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ABSTRACT

Pyrolysis is one of the potential routes to harness energy and useful chemicals from biomass. The major objective of biomass pyrolysis is to produce liquid fuel, which is easier to transport, store and can be an alternative to energy source. The yield and composition of pyrolysis oil depend upon biomass feedstock and operating parameters. It is often necessary to explore about the effect of variables on response yield and instinct about their optimization. This study reviews operating variables from existing literature on biomass pyrolysis. The major operating variables include final pyrolysis temperature, inert gas sweeping, residence times, rate of biomass heating, mineral matter, size of biomass particle and moisture contents of biomass. The scope of this paper is to review the influence of operating parameters on production of pyrolysis oil.

Contents

1. Introduction

Pyrolysis is thermal cracking of biomass feedstock without or with limited supply of oxidant-yielding volatile products and solid residue. Usual temperature of pyrolysis operation ranges within 500–800 °C. Gas, liquid, and char are three major products of pyrolysis process. The relative amount of each product depends upon operating parameters, properties of biomass and type of pyrolysis process. Usually, decomposition of biomass at medium temperature (400–550 °C) favors the production of liquid oils at short residence times. At higher temperatures, probability for production of gaseous products increases. At low temperature, char is a dominant product [1]. According to existing literature on pyrolysis, yield of liquid oils can be divided into three temperature ranges (i) fast pyrolysis ($\geq$ 500 °C) (ii) slow pyrolysis (low rates of biomass heating) and (iii) low temperature carbonization ($\leq$ 400 °C) [2–4]. As major application of carbonization is to

* Corresponding authors. Tel.: +92 42 53 93 149.
E-mail addresses: sweeetsanwal@yahoo.com (J. Akhtar), noraishah@cheme.utm.my (N. Saidina Amin).
[1] Tel.: +60 7 553 5579.

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produce smokeless fuels [5], this review does not include discussion on carbonization

Flash pyrolysis is currently a widely accepted technique for biomass liquefaction in which decomposition of biomass occurs at higher temperature for short residence times-purposely to avoid any re-polymerization of decomposed products. Fast pyrolysis usually requires dried feedstock (< 10% moisture contents), crushed biomass particles usually in size range of ~2–3 mm to expose particles for necessary heat transfer, rapid heating of biomass and quenching of hot pyrolysis vapors. According to literature, yield of pyrolysis oils range from 40% to 75% of dried biomass and is dependent on operating parameters [6–9]. In fast pyrolysis, product yields are sensitive to pyrolysis temperature variations, biomass types, heat transfer mechanism, size of feed particles, and residence times. Liquefaction by fast pyrolysis can be divided into three steps (i) biomass processing (ii) biomass decomposition (iii) quenching and separation. Drying and size reduction are usual practices for step (i). Second and third steps include pryolyzers, cyclone separators, and condensers. Biomass derived pyrolysis oil often requires up gradation to enhance its stability and hydrocarbon contents [10].

Previously, researchers have reviewed biomass pyrolysis processes [11–15]. Meier and Faix [16] summarized updates for applied pyrolysis of lignocelluloses biomasses. Bridgwater and Peacocke [17] described characteristics of fast pyrolysis and history of major processes developed since 1970. Babu [11] explained chronological developments in theoretical study on kinetic modeling, heat and momentum transfer for conventional and plasma pyrolysis. Bridgwater [13] discussed design considerations for optimized operation of pyrolysis reactors. Bridgwater [1] explained the generation of electricity from combustion, gasification, and fast pyrolysis of biomass. These reviews covered mainly the state of the art developments for pyrolysis reactors, optimization procedures, developments of pyrolysis systems over different countries and industrialization of pyrolysis processes. However, review for detail concept of processing parameters that influence the yield of pyrolysis oil from pyrolyzers is missing from literature. Since properties of bio oil such as viscosity, composition and HHV depend upon processing parameters [18], it is essential to optimize operating parameters to produce good quality liquid oils. In this review, we discussed in details on processing parameters and their optimization. Following section, explains about the effect of operating parameters on pyrolysis oil yield. These parameters include temperature, residence times, and biomass types, size of particles, mineral matter, and moisture contents of biomass.

2. Effect of processing parameters on liquid oil yield of pyrolysis processes

During pyrolysis, biomass undergoes through primary and secondary reactions involving heat and mass transfer mechanism. Primary reactions include decomposition of cellulose, hemicelluloses, and lignin present in biomass, which lead to the formation primary products and intermediates. These intermediates species further undergo into secondary cracking. Pathways for first category include dehydration and charring reactions while that of second are decomposition and volatilization of intermediates. Pyrolysis products obtained in such competitive reactions are very sensitive to operational variations and biomass type [15]. Parameters play major role to define composition and properties of pyrolysis products. Since biomass is composed of cellulose, hemicelluloses, and lignin, the extent and rate of thermal fragmentations of these components depends upon operating parameters [1]. During pyrolysis, many factors affect the nature of products. These may be summarized as type of biomass, residence times, percentage age moisture in biomass feed, temperature, pressure conditions (atmospheric, vacuum), size of feed particles and rate of biomass heating. They efficiency of a pyrolyzed also effects composition of products. Here we focused on operational parameters of pyrolysis systems. Optimization of reaction conditions can enhance the yield of pyrolysis products to any of three fuels of pyrolysis such as pyrolysis oil, gas, or solid char [19]. These parameters impart significant effect on the composition of pyrolysis products. Operating parameters are summarized in following subsections.

2.1. Temperature

The basic role of temperature is to provide necessary heat of decomposition to fragment biomass linkages. Modifications in the products composition measure the capability of temperature to decompose the biomass. At low temperature (< 300 °C), decomposition mainly occurs at heteroatom sites within biomass structure which results in production of heavy tars. While at high temperature (> 550 °C), massive fragmentation of biomass species cause the extremely high molecular disordering which results in production of numerous types of compounds. At such high temperature, both the primary and secondary pyrolysis reactions modify the product composition. There seems a tradeoff between biomass conversion and secondary decomposition for liquid oil production. Adjustments of reaction temperatures to optimize char and secondary decomposition will be helpful to obtain high liquid oil yields. Numerous experimental studies that have discussed the role of temperature on liquid oil yield are [6,8,20–26]. Biomass conversion efficiency increases with increase in temperature, which is mainly due to extra energy inputs available to break the biomass bonds. In experiments, biomass conversion is often measured indirectly by subtracting mass of char residue from initial biomass sample. For temperatures ≤ 300 °C, biomass conversion efficiency remained within 0–20% as observed in weight loss curves of biomass decomposition [27]. Percentages written in this review are weight percentages unless otherwise mentioned. Fig. 1 shows the weight loss behavior of different biomasses. Bulk conversion of biomass to its fragments usually occurs in the temperature range of 300–400 °C, which accounts to ~80–90% of total conversion [28]. However, lignin decomposes over wide temperature range unlike cellulose and hemicelluloses. Moreover, some compact biomasses types

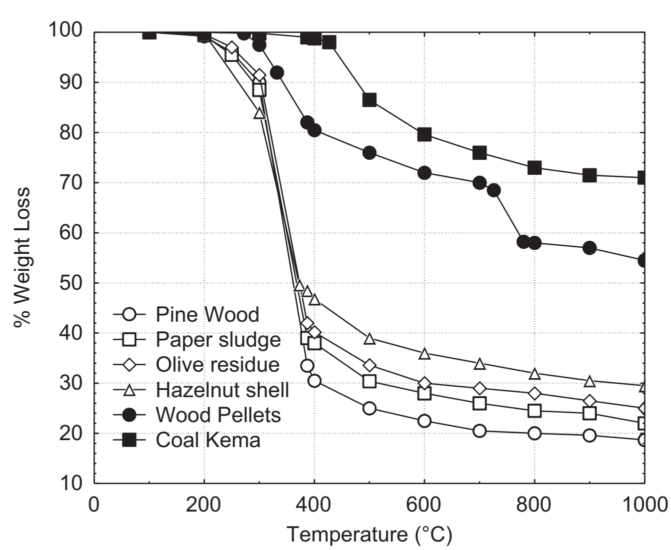


Fig. 1. Weigh loss characteristic of different biomass types [28].

continue to decompose slowly even beyond 500 °C (see Fig. 2). Solid mass obtained after initial pyrolysis stage is the semi coke. Increase in pyrolysis temperature > 400 °C causes further degradation of semi coke mass [25]. Increase in temperature from 400 °C to 700 °C decomposed 11.82% extra soybean cake during fast pyrolysis [7]. Similarly, in case of sunflower oil cake flash pyrolysis, 10.7% extra conversion was observed by increasing final temperature from 450 °C to 700 °C [29]. However, Ozbay et al. [22] observed slightly higher decompositions (17.5%) during rapid pyrolysis of cottonseed cake within same temperature interval (400–700°C). It is noticeable that biomass conversion is sequentially dependent upon temperature increase.

Final pyrolysis temperature affects the both oil and composition of liquids significantly. In general, the oil yield reaches a maximum in temperature range 400–550 °C before moving down the hill with further increase in temperature [7]. The variations in final temperature that give the maximum oil yield are due to the biomass type and operational differences. For instance, pyrolysis of sunflower cake yielded the maximum of 41% liquid oil at 550 °C [29]. While maximum of 66.89% organic liquids were produced from pyrolysis of hardwood samples at 532 °C in fluidized bed pyrolyzer [30]. Literature reports temperature to obtain maximum oil yield for different biomass. For example, (i) 550 °C for esparto biomass except for very high heating rates (68.5% oil yield) [31] (ii) 500 °C for safflower seed press cake (33.8% oil yield) [32] (iii) 550 °C for maximum oil yield (57.7%) from fast pyrolysis of linseed (iv) 530 °C for pyrolysis of soybean cake (41% oil yield) [7] and (v) 550 °C for sunflower press bagasse pyrolysis (52% oil yield) [33,34]. These results suggested that temperature in 500–550 °C range was suitable to obtaining maximum liquid yield. Differences

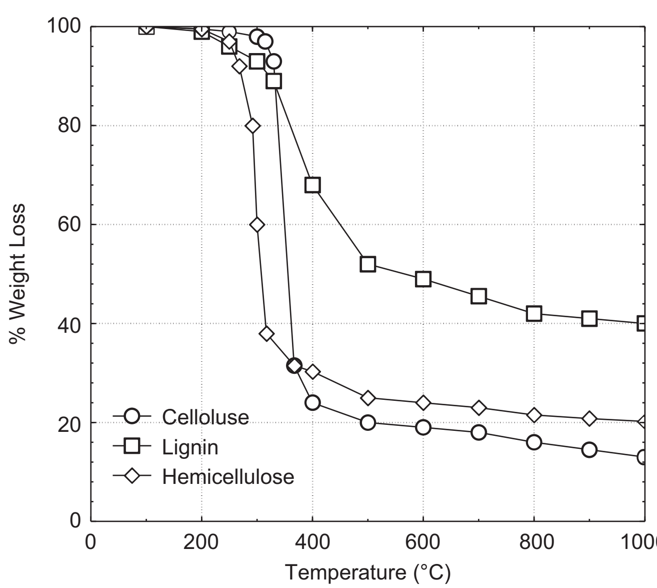


Fig. 2. Weigh loss characteristic of cellulose, lignin, hemicelluloses [28].

in weight percent of obtained liquid yield corresponds to the variations in biomass types and operational conditions. Nevertheless, at higher temperatures (> 600 °C) secondary decompositions dominate which increases the yield of gas product at the cost of char and liquid oil yields. According to Shen and Gu [35] rise in temperature (from 430 °C to 730 °C) enhanced the yield of gases while the oil yield declined for temperature > 570 °C. Proposed mechanism in the same study suggested that the precursors for gas formation were hydroxyactones (HA), hydxoryactaldehyes (HHA), 5-hydroxymethyl-furfurals (HMF-5), furfurals (FF), glyceraldehydes (GA), and pyruvaldehyes (PA) which usually are final products of biomass liquefactions. This shows that gases originate more from secondary decompositions than from primary biomass pyrolysis reactions. Thus, secondary decompositions depress liquid oil yield more than that of char. Decrease in char amount with temperature rise is mainly attributed to better biomass conversion [7] that are due to primary reactions of pyrolysis. However, secondary decomposition of char and gases also give non-condensable gaseous products by means of Boudourad and water gas reactions [36,37]. Overall, char to gas type reactions can be considered negligible compared to primary biomass conversion reactions. Various suggestions have been proposed to inhibit the secondary decomposition of tars. Rapid quenching of pyrolysis products is common practice applied in fast pyrolysis processes [17,38,39]. Sweeping away of tars produced during the pyrolysis by inert gases is also supportive to enhance liquid oil yield [29,40,41]. Moreover, washing of inorganic metals from biomass feedstock is also helpful to enhance pyrolysis oil yields as metals act as catalyst to support secondary reactions.

Bio oil composition varies remarkably due to temperature variations [42]. It is well know that pyrolysis oils are complex mixture of organic compounds from different chemical groups. Briefly the classes of organic groups found in pyrolysis oils are summarized as [43], (i) *n*-alkanes and L-alkenes (ii) monoaromatic hydrocarbons (iii) aromatic compounds (iv) aliphatic and aromatic nitriles (v) Carboxylic acids (RCOOH) (vi) long chain aliphatic amides and steroids and (vii) polycylic aromatic hydrocarbons (PAHs). Table 1 shows the composition of major compounds found in pyrolysis oils and their dependence on temperature. At lower temperatures majority of compounds in liquid fraction of pyrolysis are derivatives of functional groups present in biomass. Fu et al. [44] observed aliphatic alcohols, condensable/non-condensable phenols and carboxylic acids as major functional groups during low temperature (< 350 °C) pyrolysis of wood. Sanchez et al. [43] found carboxylic acids, phenols, *p*-cresol, and 1H-indole as major compounds during pyrolysis of sewage sludge. Concentration of these compounds reduced gradually from temperature 350 °C to 950 °C and that of benzene, toluene, styrene, and pyridine swelled during same temperature interval. As the final temperature of pyrolysis increases, the functional group containing compounds experience secondary cracking thus producing more stable species. For example, percentage yield of acetaldehyde, methanol, propanol,

Table 1
shows the composition of major compounds found in pyrolysis oil and their dependence on temperature.

Pyrolysis Temperature (°C)	Biomass type	Liquid oil composition (qualitative)	Ref.
300	Wood	Guaiacyl acetone, Levoglucosan, 5-(hydroxy-methyl)-furaldehyde-(2), Levoglucosenone, Hydroxyacetaldehyde, Acetic acid, Hydroxyacetone, Furan-(5H)-2-one, 2-furaldehyde	[45,46]
552	Yellow pine Tobacco stalk	Acetaldehyde Methanol, Acetone, Methyl acetate, Guaiacol, 4-methyl-guaiacol, 2-butanone, Acetic acid, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, Furfural, Furfurylic alcohol, 2,6-dimethoxyphenol, 2-methyl-2,6-dimethoxyphenol, Undetermined, Furan, Acetic acid, Hydroxyacetaldehyde, Propanal, Furfural	[47]

and acetone gradually decreased to almost zero by increasing temperature from 530 °C to 850 °C during pine sawdust pyrolysis [25]. Destruction of functional species leads the formation of secondary liquid intermediates such as benzene, naphthalene, cresols, and phenols. Concentration of these compounds starts mounting at intermediate temperatures reflecting their high stability. Horne et al. [42] found much higher concentrations of benzene, toluene, di-methyl benzene, and ethyl benzene at 550 °C compared to their concentrations at 400 °C. At higher temperature (> 700 °C) formation of polycyclic aromatic hydrocarbons (PAHs) such as pyrene, phenanthrene, anthracene, naphthalene dominates and their concentrations mounts up with temperature rise. The concentration of water also increases with temperature during the pyrolysis. In general, high temperature enhances the carbon contents of the bio oil compounds and reduces the oxygenate concentration because of decarboxlation and dehydration reactions Table 1.

2.2. Vapor residence times

Generally, it is accepted that short residence times are suitable for production of liquids from pyrolysis. At pyrolysis conditions, vapors are susceptible to secondary cracking or repolymerization. To minimize decomposition and coking of tars, low temperatures and residence times are preferable [48]. Vapor residence times of few seconds to few minutes are often recommended to obtain optimum yields of bio oil through pyrolysis. However, at very short residence times, it is doubtful to conceive complete conversion of biomass due to heat transfer difficulties at particle surface. Residence times for decomposition of biomass particles must be longer than the vapor residence times to obtain higher yields and biomass conversion [14]. Biomass conversion, liquid oil yield, and quality of liquid oil produced during the pyrolysis make it difficult to optimize residence times properly. As described in Bridgwater et al. [1], researches on pyrolysis of biomass mainly focused on achieving high liquid oil yields and little on oil quality. High temperatures at relatively longer residence times are suitable for producing oxygenate free bio oil. This area need to be explored to incorporate both the high yield and the better quality of oil in one operation rather than existing two stage method i.e., (i) pyrolysis and (ii) up gradation of oil. These issues reflect that merely shorting of residence times may not be a proper solution to obtain high liquid yields. Optimization of residence times considering broad range of variables may help to obtain better quality liquid oils. There can be few considerations that may support to optimize residence times of pyrolysis process which include (i) size of the biomass particles (optimization of burning times) (ii) characteristics of bio oil required (iii) maximization of biomass conversation (temperature regulation) (iv) rapid heating rates of biomass (v) sweeping of tars with a suitable inert gas seems be a better option to inhibit cracking or repolymerization reactions.

2.3. Size of feed particles

Biomass being poor conductor of heat often poses heat transfer difficulties during pyrolysis. Influence of size of feed particles is considered important on the yield and properties of liquid oil produced and to minimize heat transfer problems. Understanding the effect of particle size distributions on pyrolysis products yields may help to optimize residence times [23]. In general, small particle sizes are preferred in rapid pyrolysis systems. This may be due to the reason that smaller particles heat up uniformly. Moreover in case of larger particles, poor heat transfer to the inner surfaces will lead to low average particle temperatures and hence expected yield of liquids may decrease. Larger particles require high apparent activation energies, which can be attributed to heat transfer limitations [49]. General specifications for different pyrolysis systems have been suggested such as < 200 mm for rotating cone pyrolysis, < 2 mm for fluid bed systems, < 6 mm for circulating fluid beds [17]. Nevertheless, specific data for feed sizes of different biomass types to be used in a pyrolysis system is missing from literature. For example, Beis et al. [19] reported particle size 0.425 mm yielded the maximum oils during pyrolysis of safflower in fixed bed compared to any higher feed sizes. Nurul Islam et al. [50] recommended order: uncrushed > 1–2 cm > 1 cm for particle size during pyrolysis of municipal solid waste in fixed bed pyrolysis. Onay et al. [51] reported that medium particle size ($0.6\ \mathrm{mm} < dp < 0.85\ \mathrm{mm}$) yielded maximum liquids compared to smaller (< 0.4 mm) and larger (> 1.8 mm) feed sizes in fixed bed pyrolysis of rapeseed. Similarly for fixed bed pyrolysis of hazelnut, feed particle size of 0.425–0.6 mm yielded maximum liquids compared to $0.225 < dp < 0.425$ or $dp > 0.85$[52]. According to Aylon et al. [53], yield of liquids oils was different for fixed bed and moving bed reactors even for same average size (2 mm) of waste tire feed. These conflicting information on biomass feed sizes make it difficult to generalize the size of feed particles for a specific pyrolysis system.

Unexpected higher yield of liquids with larger biomass particles are possibly due to difference in the types of biomass used during pyrolysis. Bulk density and oxygen contents of biomass may have some relationship with heat transfer mechanism and rate of pyrolysis reactions. Significant effect of particle size distributions on liquid oil yield in pyrolysis of coal and oil shale suggested the heat transfer limitations were prominent in such biomass types. For biomasses such as sunflower bagasse [54], grape baggase [55] and rapeseed[56], the maximum liquid oil yield was obtained in case of intermediate particles size distributions. However, in all these cases, the difference among the liquid oil yield was low which indicated the low interference of particle size distributions on liquid oil yield. Presence of higher oxygen contents both in sunflower baggase and rapeseed [57,58] shows that these are reactive species and relatively independent of heat transfer limitations. While strong dependence of coal or oil shale upon the particle size distribution for liquid oil yield mainly attributes to their less oxygen contents and compact biomass structure.

Finally, useful size of the feed particles may vary depending upon the type of biomass and type of pyrolzer. Size reduction of biomass feed is associated with penalty for cost of grinding. In pyrolyzers it would be wise to use larger feed size. However, this cannot be an absolute criterion. Infect a combined relationship that can minimize the cost of grinding and operational times for a given biomass can suggest particle size distributions properly. Maximization of liquid oil yield should remain the main window to judge effect of particle size distributions.

2.4. Biomass heating rates

Rate of biomass heating is another important factor that defines the types of decompositions products. In fast pyrolysis, heating rates are usually higher than that in conventional process. Fast heating rates cause quick fragmentations of biomass and enhances the yield of volatiles. Enhancement in volatiles is mainly because of extra tar decompositions at high heating rates [59]. According to Seebauer et al. [60], yield of products from fast pyrolysis depends upon two competing reactions occurring in decomposing metaplast: the tar evaporation and char formation. At high heating rates, high yield of liquids oil mainly owes to short time available for secondary reactions: tar cracking and repolymerization. However, at high temperatures gases are the

major products. Heating rates of up to 1000 °C/min have been suggested [61]. For liquefaction of biomass, fast heating rates are usually preferred. Rapid heating rates reduce the heat and mass transfer limitations. Rapid heating enhances volatiles abundance by fast endothermic decomposition of biomass, thus minimizes time available for secondary reactions like tars cracking or repolymerzation [62]. This results in fast removal of high molecular tars and volatiles from the decomposing biomass matrix leaving low char amounts.

In order to elaborate, the effect of heating rate on the yield of liquids various researches have been conducted [6,7,23,31,32]. Synergetic effect of heating rates on liquid oil yield has been observed in many studies. Salehi et al. [63] reported that rapid heating of sawdust sample increased the liquid oil yield from 500–700 °C/min at 500 °C while for intervals 100–500 °C/min and 700–1000 °C/min no synergetic effect on liquids production was observed. Once heat and mass transfer limitations are overcome, further increase in heating rates may not improve liquid oil yields. It was not clear as to why liquid oil or volatiles yield could not be improved during 100–500 °C/min interval possibly due to non-homogenous heating of sample. Uzun et al. [23] reported 23.36% rise in liquid oil yield by increasing heating rates from 5 °C/min to 700 °C/min for rapid pyrolysis of soybean cake. Unlike Salehi et al. [63], oil yield for soybean cake pyrolysis continuously increased for the observed heating rate interval (5–700 °C/min) in their study. Ozbay et al. [22] observed that liquid oil yield was increased at faster rates for initial heating rate interval (0–300 °C/min) compared to the variations from 300–700 °C/min during rapid pyrolysis for cottonseed cake. This observation was similar to that reported in Uzun et al. [23]. Similarly Sukiran et al. [64] observed change in heating rates from 10 °C/min to 50 °C/min enhanced liquid oil yield more than from 50 °C/min to 100 °C/min.

Higher heating rates also affect the optimum temperature for obtaining liquid oil yield. For example, Debdoubi et al. [31] pyrolyzed esparto biomass at different heating rates (50 °C/min, 150 °C/min, 250 °C/min) for temperature range of 400–700 °C. They found that optimum temperature for heating rates of 50 °C/min and 150 °C/min was 500 °C yielding 45% and 57% liquid oil, respectively. However, for 250 °C/min, the maximum oil yield was shifted to 550 °C/min. Similar temperature shift was also observed for slow pyrolysis of wood barks and for fast pyrolysis of rapeseed [51]. This behavior may be due to the reason that high heating rates generate more volatiles comparatively and biomass fragmentation continues for larger range of temperature. In addition, because biomass bed temperature rises faster than the volatiles removal rates at high heating rate. Sensoz et al. [32] could not observe any temperature shift for variation within interval 10–50 °C/min, possibly due to low heating rates overall compared to those studied by Debdoubi et al. [31]. It is also noticeable that amount of water contents in aqueous products decreases at higher heating rates thus producing better quality bio oil [7,22]. Rapid heating probably inhibits secondary condensation and dehydration reactions. Moreover, oxygen contents of final aqueous product decrease at higher heating rates [31]. This suggests that the formation of oxygen containing gases such as CO_2 or CO increases for high heating rates [60].

2.5. Effect of sweeping gas

The reactive environment of pyrolysis process can influence the type and composition of all products. The interaction of escaping pyrolysis vapors with surrounding solid environment provokes secondary exothermic reactions that lead to the formation of char. Pyrolysis conditions that support rapid mass transfer are useful to minimize these reactions such as vacuum pyrolysis, fast purging of pyrolysis vapors, rapid quenching of hot vapors and small feed size [65]. The use of inert gases is common practice for rapid purging of hot pyrolysis vapors such as N_2, Ar and water vapors. The most of the studies employed N_2 gas flow due to cheapness. Passing N_2 through process reduces the residence times of pyrolysis vapors. Thus N_2 flow inhibits the possibility of recommendation, repolymerization of vapors and maximizes the liquid yield [7]. It is notable that nitrogen gas only pushes the hot vapors out of the reaction zone. Rapid quenching of thermally cracked pyrolysis vapors is then necessary to stop secondary reactions occurring in hot vapors [66].

From the literature, it is assumable that the liquid oil yield is not influenced by sweep gas flow rates. Sweep gas flow can be considered as secondary parameter for production of liquid oil from fast pyrolysis. Acikgoz et al. [67] observed the 3% more liquid oils by increasing nitrogen flow rates from 50 cm^3/min to 100 cm^3/min. Demiral and Ensoz [52] found only 3.3% extra liquid oil yield by varying nitrogen flow rate within 50–150 cm^3/min interval. Similarly, Putun et al. [68] observed 3% more liquid oils at 200 ml/min than at 50 ml/min of nitrogen flow. It is also notable that very high flow rates of sweep gas actually decreased the total oil yield [52]. Usually low gas velocity is sufficient to attain maximum oil yield [69]. Possible reason to this point is that high sweep gas velocities support gas yield. At high gas velocities, the volatiles leave the system without effective condensation, which results in gas formation. This behavior of producing more gas amounts at high sweep velocities can be observed in [32].

Other than nitrogen, steam is used as sweep gas as well as medium for pyrolysis. Addition of steam meets dual objectives during pyrolysis (i) sweeps the hot pyrolysis vapors (ii) favors the formation of liquids by reacting gases products and solid char [68,70]. Steam pyrolysis is usually more suitable for production of liquid oils compared to N_2 gas sweeping. This is because N_2 gas sweeping produces more gaseous products than steam pyrolysis. However, addition of steam may increase oxygen contents of pyrolysis oil. Putun et al. [68] compared the effect of nitrogen and steam atmospheres on the fast pyrolysis of rice straw. Steam pyrolysis produced 5.63% more liquids than by nitrogen sweep gas assisted pyrolysis. Higher steam velocities (2.7 cm/s) were favorable for inhibition of gases and char products compared to lower ones (0.6 cm/s). Minkova et al. [70] made similar observations during pyrolysis of agricultural and forestry waste samples in steam and nitrogen environment. In their study, steam pyrolysis produced maximum amount of water-soluble, tars while gases, and char was higher in nitrogen sweeping. Other than yield, composition of liquids also varies by changing steam flow rates. Water condensates extract water-soluble components both from tars and gaseous products thus shrink the volume of undesired products. During pyrolysis, volume of aliphatic, aromatic hydrocarbons and asphaltenes rises while polar compounds are discouraged at higher steam flow rates. Moreover, steam is expected to enhance generation of free radicals by breaking the bonds at heteroatom sites. These free radicals further form different end compounds such as H_2S, CO, CO_2, saturated hydrocarbons, and aromatic compounds [71].

Gercel et al. [34] carried out a detail study on the effect of nitrogen flow rates in fast pyrolysis of sunflower pressed baggase at final pyrolysis temperatures of 400 °C, 500 °C, 550 °C, and 700 °C. Variations in liquid oil yield were observed at 25, 50, 100, 200, and 400 cm^3/min at each individual temperature. Observations are summarized as follows.

- Maximum of liquid oils were observed at pyrolysis temperature of 550 °C for nitrogen flow rates of 50 cm^3/min. For 500 °C and 550 °C, liquid oil yield was increased for nitrogen flow rates interval of 25–50 cm^3/min. Liquid oil yield was actually

decreased for higher values of nitrogen flow rates (50–400 cm^3/min).

- Liquid oil yield for final pyrolysis temperatures of 400 °C and 700 °C was much lower compared to 500 °C or 550 °C. This suggested that final pyrolysis temperature acted as prime parameter while affect of nitrogen flow rates was auxiliary. Liquid oil yield was the lowest in case of 700 °C operation possibly due to high degree of gasification.
- Synergetic effect was observed on liquid oil yield for all of the nitrogen flow rates (25–400 cm^3/min) both for final temperature of 400 °C and 700 °C.

This study could not observe the marked effect of sweep gas on the yield of liquid oil. This behavior is common in many other investigations as well [7,29]. However, sweep gas flow rates are supportive for liquid oil yields in pyrolysis of compact biomass species such as coal or oil shale. The major differences are the oxygen contents and bulk density of the biomass. Higher the bulk density and lower the oxygen contents, the more will be the effectiveness of the inert gas sweeping. This owes to the mass transfer restrictions to volatile evolutions during pyrolysis. Inert gas sweeping is usually not much effective for biomass types that are relatively reactive and are loosely structured. It is noticeable that low flow rates of sweeping gas usually are usually sufficient to enhance the amount of liquids in fast pyrolysis operations. As discussed earlier, the reason to this point is the reduction in residence times of the pyrolysis vapors. Gas sweeping drags these hot vapors quickly out of the pyrolysis zone, which helps to stop secondary reactions such as condensation and repolymerization. However, the oil yield usually is inhibited by the higher sweep gas flow rates. Reason to this point is not much clear in the literature. Instead, it is observed that higher flow rates of sweeping gas produced more of gases compared to that of low flow rates [23]. This suggests that higher sweep flow rates also stop reactions among lighter products of pyrolysis, which are useful for production of liquids. This can be possible explanation of low liquid oil yields at higher flow rates of sweeping gas.

2.6. Effect of biomass type

Biomass is composed of lignin, hemicelluloses, cellulose, and small fraction of inorganic matter. The relative mass ratios of the both organic and inorganic compounds vary in different biomass types. The composition of products of pyrolysis depends very much on these compositional variations in biomass species. Second, extent of decomposition depends upon the biomass composition.

Ease of decomposition among three major components (cellulose, hemicelluloses, and lignin) is attributed to their structural stability. Pyrolysis of cellulose or hemicelluloses produces more oil yields than lignin. Yang et al. [72] reported the weight loss behavior of hemicelluloses, cellulose, and lignin. Maximum weight loss was observed for cellulose (94.5%) and hemicelluloses (80%) at 400 °C and 268 °C, respectively. While only 54.3% of lignin was volatilized at 900 °C. It is clear that final temperature to obtain maximum oil yield depends upon biomass components and that lignin contributes to the major portion of char residue during pyrolysis of a lignocelluloses biomass. Gani and Naruse [73] reported similar observations for pyrolysis of cellulose, lignin, bark, rice husk, and corn stalk. Second, the structural differences among major biomass components cause compositional variability in the pyrolysis products (Table 2). Presence of oxygen contents and heteroatom are other factors that affect the reactivity of biomass species during pyrolysis. In general, higher the oxygen and the heteroatom, more is the reactivity of biomass. Some studies reported relatively low effect of oxygen contents on reactivity of biomass during pyrolysis. For example, Tatterson et al. [74] investigated the effect of different feedstock (Montana lignite, Minnesota peat, and Illinois bituminous) on the yield of pyrolysis products. They observed maximum liquid yield from Minnesota. Conversion of Montana lignite was the lowest in spite of the presence of high amount of oxygen. Moderately reactive bituminous coal yielded higher amount of gases that may owe to the presence of high sulfur contents. This suggested the independence of liquid oil yield and biomass conversion on oxygen contents of coal types Table 2.

2.7. Influence of mineral matter/metal ions

Biomass contains trace amounts of inorganic compounds metals (K, Na, P, Ca, Mg) and extraneous organic materials (4–10%) which appears in pyrolysis ash. Composition of mineral matter is an important parameter for secondary pyrolysis reactions and influences the reactivity of pyrolysis char. In general, mineral matter decreases the amount of liquid oils and tends to increase char and gas formation. This is because inorganic materials speed up dehydration and charring reactions during both primary and secondary pyrolysis. The variations in pyrolysis products distribution are also dependent upon the composition and type of mineral matter in biomass. According to Franklin et al. [78], the presence of Kaolinite clay mineral during pyrolysis of bituminous coals promoted secondary cracking in liquids oils but not in char. They suggested that the relative ease of accessibility of light liquid fractions to the pore structure of clay materials promoted oil cracking. Carbonates and metal oxides are reactive to oxygen bearing functional groups in biomass. Presence of alkaline species in mineral matter enhances interaction among alkali carbonates, –COOH and –OH functional groups thus forming alkali-oxygen surface clusters. These reactive points promote the secondary decomposition reactions [79]. Similarly, the presence of silica or metal chlorides lowers the yield of oil [80]. Oztas and Yurum [79] observed that washing of silicates from bituminous coal sample significantly enhanced its swelling index (SI). SI defines the coking or pyrolysis potential of a biomass or coal. This suggests that mineral matter removal is important for SI enhancement. Moreover, the biomass ash can cause fouling and corrosion of pyrolyzer. Low melting point constituents in ash can induce agglomerization of pyrolzer bed materials. Silica seldom softens under pyrolysis conditions but its presence in the bed cause softening of biomass particles and changes their thermoplastic behavior. Nik-Azar et al. [81] showed that tar yield was dependent upon the reactivity of

Table 2
Dependence of pyrolysis oil composition on major components of biomass feed.

Components	Pyrolysis oil products	Ref.
Cellulose	Oligosaccharide, Cellobiosan, Glucose, Glyoxal, 1,6-Anhydroglucofuranose, Levoglucosan, Formic acid, Acetic acid, Ethylene glycol, Diacetyl	[75]
Hemicellulose	Rhamnose, Arabinose, Xylose, Mannose, Vanillin, Syringaldehyde	[76]
Lignin	Guaiacol, 1,2-dimethoxybenzene, 2.4-dimethylphenol, 6-methyguaiacol, Catechol, 2,3-dihydroxytoluene, 4-ethylguaiacol, 4-vinylguaiacol, Eugenol, 4-ethyl-6-methylguaiacol, 1,2-dimethoxybenzaldehyde, Vanillin, 3,4-dimethoxy-4-propylbenzene, Iseugenol, 1,2-dimethoxy-4-propenylbenzen	[77]

mineral matter types. Presence of high amounts of K, Na, and Ca metals greatly reduced the tar yields indicating the strong effect of alkali metals on secondary decomposition of tars. Acid washed samples yielded the maximum tar yield (61%). Acid washed samples has the lowest concentration of K, Na, Ca metals compared to both original beech wood sample and metal impregnated samples. The high catalytic reactivity of metal cations K, Na towards cracking of heavier compounds is the major reason for low tar yields. High yield in case of acid washing also owes to swelling of wood sample pores, which inhibits the passage of tars through biomass surfaces. Raveendran et al. [82] reported that all of the biomass samples showed higher liquid yields on demineralization of mineral matter except for biomass types, which have high amounts of lignin and K metal. K metal is supposed to facilitate gas and charring reactions. They proposed a correlation for the effect of mineral matter constituents (K, Zn) and amount of lignin on the volatiles yield of biomass pyrolysis (Eq. 1).

$$\Delta V = -0.964(L_{1.095} \times X_k^{1.3727} \times X_z^{0.0996}) + 7.192 \quad (1)$$

where L, X_k, X_z are the amount of lignin and K, Zn are fractions in the mineral matter. ΔV is the change in the volume of volatiles. It is clear that higher amounts of lignin and corresponding metals in mineral matter will reduce the amount of volatiles. This discussion suggested that mineral matter leads to the formation of char and gases but inhibits the production of liquid oil during pyrolysis. The major reasons for this behavior are the secondary pyrolysis reactions and easier diffusion of tars inside the mineral matter pores.

To inhibit deleterious role of mineral matter during pyrolysis, washing of biomass is often useful for liquid oil production. Washing of mineral matter is one of the suitable options that include acid, hot, and cold-water washing [1,83]. For comparison, the hot water washing is capable of removing major components of mineral matter. While, acid washing is more suited to remove acid soluble or alkaline species present in biomass. Acid washing also leads to the partial hydrolysis of biomass components. Gonzalez et al. [84] reported that acid washing removed more than 70% of inherent minerals from poplar wood and approximately 65% of those from giant reed canes. According to previous studies, hot water technique is an appropriate method to wash mineral matter for wide range of biomass species [85].

2.8. *Effect of initial moisture contents of biomass*

Green biomass usually contains about 50–60% moisture contents. It is necessary to dry biomass because the pyrolysis systems can handle biomass typically having < 30% moisture. Ambient air solar drying can reduce moisture contents in the range of 3–12%. Alternatively, waste heat drying and mechanical dryers are also useful. Initial moisture contents influence both the behavior of biomass during pyrolysis and physicochemical properties of pyrolysis oil. During pyrolysis, heat is utilized in endothermic evaporation of moisture contents present in biomass particle and decomposition reactions as discussed in [11]. The rate of moisture removal depends upon the rate of biomass heating and final pyrolysis temperature. The initial moisture contents increase (i) the energy inputs to dry biomass and (ii) the pyrolysis reaction temperature. Very high moisture contents in biomass slowdowns the rate of biomass heating. For example, biomass with 40% initial moisture contents required extra 1120 kJ/kg dry wood energy to commence pyrolysis reaction compared to dry wood sample [15]. Moreover, the rate of biomass heating and final pyrolysis temperature to obtain maximum oil yield show a slight dependence on initial moisture present in biomass sample [86].

The amount of water contents and the yield of pyrolysis oil show a marked dependence upon the initial moisture contents. Increase in water contents seems logical, as the moisture present in biomass directly adds into aqueous products of pyrolysis. Demirbas [86] observed approximately 3% increase in water amount for spruce biomass samples due to initial moisture variations. For liquid oil yield, the role of initial moisture contents seems beneficial. Initial moisture serves two purposes (i) stabilization of the pyrolysis fragments and (ii) dissolution of soluble fragments. These two steps are helpful to achieve high liquid yield. Increase in initial moisture content leads to the increase in maximum aqueous yield. Demirbas [86] observed approximately 6% higher liquid yields with 11.5% initial moisture contents in spruce biomass pyrolysis compared to dry spruce sample. This increase owes to better stabilization of biomass fragments and the enhancement in water contents of oil due to initial moisture. The actual oil yield should not include the water contents. An appropriate criterion is to report the increase in oil amount on moisture free bases. Therefore, there was only 3% increase in bio oil contents due to spruce fragmentation. It is also notable that, profile of liquid oil yields verses temperature flows a similar trend at all moisture contents. The yield of liquid oil reaches a maximum at certain temperature afterwards lowers for higher temperatures (Fig. 3).

Composition and physical properties of pyrolysis oil are also sensitive to initial moisture contents. During pyrolysis, almost all of the initial moisture contents appear in the aqueous product fraction. At least 15% of pyrolysis oil consists of water. Water contents of aqueous yield usually lie within 18–25% range when feed moisture content is less than 10% [14]. Water contents in pyrolysis oil originate from the initial moisture contents and from the dehydration reactions. Decomposition of oxygenates present in solid feed and water–gas shift reactions also add water contents to aqueous fraction of pyrolysis [6,88]. Water lowers the fuel value of bio oil. Water contents also affect the physical properties of pyrolysis oil such as chemical stability, viscosity, corrosiveness, and pH. There is a misconception about the yield of aqueous products of pyrolysis. Total aqueous yield should not include the initial water amount. True aqueous yield of pyrolysis will be the amount of liquids produced during pyrolysis. Therefore, the meaningful aqueous yields are those reported on moisture free biomass feed basis [14,89]. Removal of water from pyrolysis oil is difficult by conventional methods. However, selective condensation can reduce water contents [1].

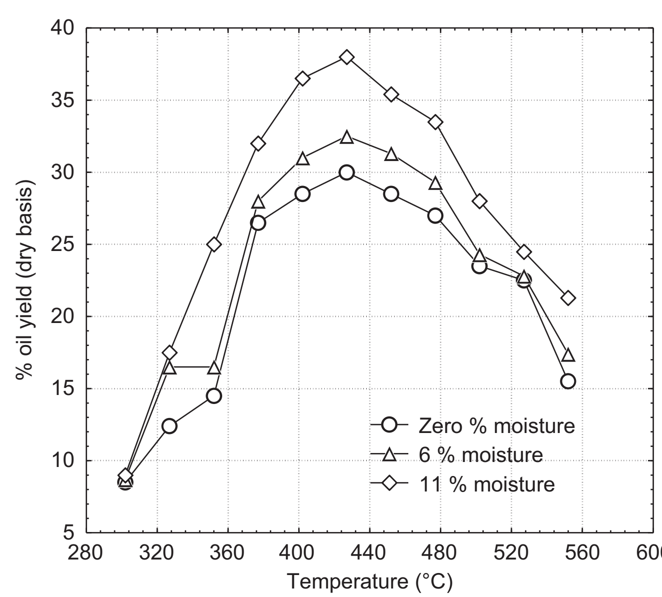


Fig. 3. Effect of moisture contents on the yield of a pyrolysis process [87].

For practical purposes, the low initial moisture contents in biomass are usually preferable. The advantages that are associated with low initial moisture contents include (i) low heat energy requirements for vaporization and commencement of pyrolysis reaction (ii) reduction in residence time and (iii) better oil quality. Water present in oil product (i) add post processing costs (ii) lowers the stability of the oil. Thus, the lowest possible water contents in biomass are advisable for pyrolysis purposes. It is also notable that completely dried biomass feedstock suffers heat transfer limitations because of its low heat conductivity. A minimum amount of initial moisture contents is necessary because water acts as reactant for biomass species and as heat transfer medium, which enhances pyrolysis.

3. Conclusion

The operating parameters of a pyrolysis process influencing composition and yield of volatiles, are classified as: (i) highly influencing parameters (ii) moderately to low influencing parameters. First category includes temperature and biomass types. Temperature is the most influencing parameter in pyrolysis of biomass. Intermediate pyrolysis temperatures (500–550 °C) usually maximize the liquid oil yield. Low and very higher temperatures lead to the formation of char and gases, respectively. Final pyrolysis temperature can cause 10–20% variations in yield of liquid oils. Final temperature range of 500–550 °C usually leads to the formation of higher yield of aqueous fraction. For loosely structured biomass this range tends to vary from 470–550°C. Lignin model compounds require higher temperature 550–650 °C. Even at very high temperature (800–900 °C), pyrolysis of lignin does not yield more than 60% biomass conversion. Biomass types and pyrolysis temperature are two major parameters for liquid oil yield. In general, cellulose and hemicelluloses tends to produce more volatiles. Lignin is hard to fragment even at higher temperature and appears in major composition of char residue. Compositional variations in biomass will modify composition and yield of pyrolysis oil. A combination of moderate pyrolysis temperature, rapid biomass heating rates, and short residence times maximizes the yield of liquid. Vapor residence times, size of feed particles, rate of biomass heating, sweeping gas flow rates, mineral matter contents, and initial moisture impart secondary effects on yields and composition of volatiles. Among these, mineral matter and initial moisture contents are negatively influencing parameters for volatiles yield and energy inputs, respectively. Heating rates and initial moisture contents both result in higher oil yields. However, the quality of pyrolysis oil is inferior compared to that obtained from low heating rates and dry biomass. Small biomass particles are preferable for uniform heat distribution. Large biomass particles lead to low biomass conversion and volatiles yield. Influence of biomass is negligible for reactive biomass species. However, heat and transfer limitations increase with particle size for stable species such as coal. Sweeping gas flow rates render only negligible to low effects for oil yield. Sweeping of gases reduces volatiles residence times, which helps to minimize secondary cracking and repolymerization of vapors. However, a rapid quenching of hot pyrolysis vapors is necessary to obtain high liquid yield. Low to moderate flow rates of sweeping gas are helpful to obtain high liquids. Nitrogen gas sweeping is the usual practice. It is well know that short residence times produce maximum liquids. Longer residence times lead to low liquid yields due to secondary reactions. However, liquid yield shows only a little decrease for longer residence times.

Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.rser.2012.05.033.

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